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<p>This report summarizes the results obtained on the H_2^{16} absorption spectrum in the spectral regions $8000-11500\text{ cm}^{-1}$ and $13500-22700\text{ cm}^{-1}$. The spectra were recorded at high resolution with a Fourier transform spectrometer using a multipath cell allowing path lengths up to 434 m. A thorough analysis has been performed and greatly improved line positions, intensities and assignments have been obtained providing a precise and complete picture of the H_2^{16} spectra in the concerned spectral regions.</p> <p>These results of important atmospheric interest will be included in the next version of the HITRAN data base. (A.W.)</p>			
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Owen R Cote'

OWEN R. COTE'
Chief, Geophysics and Space

Fred T Gilliam

FRED T. GILLIAM, Lt. Col, USAF
Chief Scientist

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STUDY OF HIGH FREQUENCY WATER VAPOR ABSORPTION PARAMETERS

Jean-Marie FLAUD and Claude CAMY-PEYRET

Laboratoire de Physique Moléculaire et Atmosphérique

Université Pierre et Marie Curie et C.N.R.S.

Tour 13, 4 place Jussieu, 75252 Paris cedex 05, France

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223/231 Old Marylebone Road, London NW1, 5th, U.K.

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Optical remote sensing and studies of the propagation of radiation through long atmospheric paths require a precise knowledge of the spectral parameters of molecular absorbers contributing to the opacity. Because of technological considerations, the first spectroscopic efforts were devoted to the mid and infrared regions. Recent advances in optics have now created a need for precise spectroscopic data from the near-infrared to the visible and the purpose of the project was to improve the spectroscopic parameters of water vapor which is, with oxygen, the main atmospheric absorber in this spectral region.

Our work during the three years period of the contract has concerned the following spectral regions :

13500 - 22700 cm⁻¹ [Ref.1,2]

8000 - 9500 cm⁻¹ [Ref.3]

9500 - 11500 cm⁻¹ [Ref.4]

and the following improvements* have been achieved as compared to the existing H₂¹⁶O data presently reported in the HITRAN data base.

Line positions.

The accuracy on the line positions measured in the present work is, for well isolated lines, varying from 0.5×10^{-3} to 2×10^{-3} cm⁻¹ depending on the spectral region; this improves greatly upon the previous data (accuracy $\approx 10^{-2}$ cm⁻¹ for the better lines).

- Line assignments.

Real progress have been made in assigning the lines. In particular many new resonating lines have been attributed and some previous assignments were found erroneous.

*We give in this first part only the salient facts of the work. Far more details, the reader is requested to refer to the Appendix where the analysis process, the theoretical problems and the results are extensively described.

- Line intensities.

The average uncertainty on the line intensities is about 6-10% (However errors up to 50% exist for heavily blended lines). The lines intensities were measured either by the curve of growth method or using the peak absorption method (See Ref.3 for details). In this way, the intensities of all the observed lines were derived and it has to be underlined again that a real improvement has been obtained : For example, the results quoted in Table V of Ref.[3] show clearly that the previous intensities listed in the HITRAN data base are in error by a factor ranging from 2 to 7.

All the results (line position and intensities) which give a precise and complete picture of the H₂¹⁶O absorption in the spectral ranges 8500 - 11500 and 13500 - 25250 cm⁻¹ have been given through diskettes to L.S. Rothman who is charge of the HITRAN data base and should be included in the next version of the base. As a whole it appears that the contract has been properly fulfilled and has produced interesting scientific results.

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APPENDIX

Detailed description of the spectral regions :

16500 - 22700 cm^{-1}

13200 - 16500 cm^{-1}

8000 - 9500 cm^{-1}

9500 - 11500 cm^{-1}

$H_2^{16}O$: Line positions and intensities between 8000 and 9500 cm⁻¹: the second hexad of interacting vibrational states: {(050), (130), (031), (210), (111), (012)}

J.-Y. MANDIN, J.-P. CHEVILLARD, J.-M. FLAUD, AND C. CAMY-Peyret

Laboratoire de physique moléculaire et atmosphérique, Université Pierre-et-Marie-Curie et Centre national de la recherche scientifique, Tour 13, 4, place Jussieu, 75252 Paris CEDEX 05, France

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Water vapor Fourier-transform spectra (resolution = 0.010 cm⁻¹) have been analyzed between 8000 and 9500 cm⁻¹. Accurate values of 441 rotational energy levels, belonging to the vibrational states (050), (130), (031), (210), (111), and (012) of the second hexad of $H_2^{16}O$, have been determined. Moreover, 500 line intensities have been accurately measured (uncertainty = 6%). To increase the number of experimental intensities (useful for atmospheric applications), we have set up a less sophisticated but faster method; this has led to the measurement of 1200 additional intensities, with an average uncertainty of about 10%.

Des spectres par transformée de Fourier de la vapeur d'eau (résolution = 0.010 cm⁻¹) ont été analysés entre 8000 et 9500 cm⁻¹. Les valeurs précises de 441 niveaux d'énergie rotationnels, appartenant aux états vibrationnels (050), (130), (031), (210), (111), et (012) de la deuxième hexade d' $H_2^{16}O$, ont été déterminées. De plus, on a mesuré avec précision les intensités de 500 raies (incertitude = 6%). Dans le but d'augmenter le nombre d'intensités expérimentales (utiles pour les applications atmosphériques), une méthode moins sophistiquée mais plus rapide a été mise au point et a permis de mesurer 1200 intensités supplémentaires, avec une incertitude moyenne d'environ 10%.

Can. J. Phys. 66, 997 (1988)

1. Introduction

For atmospheric applications, it is important to know accurately the vibration-rotation spectrum of water. As a continuation of our previous work on this molecule, this paper presents a study of the 8000–9500 cm⁻¹ spectral region. This region was first analyzed by Benedict (1), and improved results were later introduced by him in the atmospheric compilations (2). Then, using a grating spectrum of room-temperature water vapor and a Fourier-transform spectrum of heated water vapor ($T = 330$ K), both recorded with a resolution of 0.07 cm⁻¹, Flaud *et al.* (3) improved the accuracy of the energy levels. Finally, with the aid of oxygen-hydrogen flame spectra recorded on a Fourier-transform interferometer between 6400 and 7600 cm⁻¹, Camy-Peyret *et al.* (4) analyzed the $\nu_1 + \nu_2 + \nu_3 - \nu_1$ hot band and were able to determine rotational levels of the (111) vibrational state corresponding to high values of the J quantum number (up to $J = 26$). To observe new levels and to improve the accuracy of the previous results, we have studied several spectra (resolution = 0.010 cm⁻¹) recorded with the Fourier-transform spectrometer built by Brault (5) at the National Solar Observatory, Kitt Peak, AZ.

The analysis of these spectra has led to the determination of 441 accurate rotational energy levels belonging to the so-called second hexad of interacting vibrational states: {(050), (130), (031), (210), (111), (012)}.

To study high-resolution atmospheric spectra, one must know more than the wavenumbers and the assignments of the observable $H_2^{16}O$ lines; it is also important to have at hand a complete and reliable list of individual line intensities. In the studied spectral region, knowledge of experimental intensities has been somewhat poor. Let us mention one temperature-insensitive line measured by Brault *et al.* (6) (uncertainty = 10%) and 33 line intensities measured by Cherepanov *et al.* (7) (uncertainty = 10%). That is why we have first measured 500 line intensities accurately (uncertainty = 6%). Besides, to extend this set of values, we have set up and successfully tested a faster method to obtain the intensities of all the other lines pertaining to the $H_2^{16}O$ molecule. Thus, 1200 additional intensities have been measured, with an average uncertainty of about 10%. The method is described in Sect. 3, where the measured intensities are discussed.

2. Experimental details and analysis

Since numerous isotopic species of water absorb simultaneously, it is very useful to have spectra corresponding to different ratios of isotopic concentrations at one's disposal when assigning each line to a peculiar absorber, i.e., mainly $H_2^{16}O$, $H_2^{18}O$, or $H_2^{17}O$. For this reason, natural, ¹⁸O-enriched, and ¹⁷O-enriched water vapor spectra have been recorded with the aid of Brault's Fourier-transform apparatus (5). Moreover, because of the large range of line intensities, several spectra have been recorded at various path lengths and pressures, allowing us to cover a sufficiently large set of $H_2^{16}O$ optical thicknesses. Thus, it is possible to measure the intensities of strong lines (up to 2.8×10^{-2} cm⁻²·atm⁻¹) as well as very weak lines (as low as 5×10^{-7} cm⁻²·atm⁻¹) (1 atm = 101.3 kPa). The experimental conditions and characteristics of the spectra are given in Table 1.

To give an idea of the complexity of the spectrum, in Table 2 we report measured or previously computed band centers and band strengths for the main bands appearing in the studied spectral region. One can see that six interacting vibrational states are involved: they form the second hexad of H_2O , i.e., {(050), (130), (031), (210), (111), (012)}. The six corresponding cold bands have been observed, revealing numerous resonances that have complicated the assignments.

As an example, the $5\nu_2$ band could be observed owing to three strong interactions: two of them have been previously calculated by Ulenikov and Ushakova (8). These interactions occur between the levels (050)[761] and (130)[743], between (050)[660] and (210)[606], and between (050)[661] and (130)[643]. For these pairs of interacting states, the mixing of the wavefunctions is so important that the assignment of the vibrational quantum numbers to each level is difficult. Thus, at the present time, the proposed attributions are a matter of convention.

Another example of strong perturbation involves the vibrational state (060), which actually pertains to the first decad. It exhibits a quadruple interaction (3) between the levels (060)[616], (130)[652], (210)[634], and (111)[624], so that the very weak $6\nu_2$ band can be observed through seven lines, corresponding to transitions arriving at the resonant level (060)[616].

TABLE I. Experimental conditions and characteristics of the absorption spectra (1 atm = 101.3 kPa)

Type of spectrum	Unapodized resolution (10^{-3} cm $^{-1}$)	Total pressure $P \pm 1\%$ (10^{-3} atm)	Average Lorentz half-width γ^L (10^{-3} cm $^{-1}$)	Absorption path l (cm)	$H_2^{16}O$ concentration x	$H_2^{16}O$ optical thickness $x P l$ (cm·atm)
Natural	17.4	22.8	9.3	43 396	0.997	986
	14.5	1.97	0.8	43 396	0.997	85.3
^{18}O enriched	11.2	3.68	1.5	21 742	0.27 ± 0.01	21.6
	11.2	3.68	1.5	4 900	0.27 ± 0.01	4.87
	11.2	0.96	0.4	2 494	0.27 ± 0.01	0.65
^{17}O enriched	11.2	6.18	2.5	21 742	0.79 ± 0.03	106
Studied spectral region: 7900–9500 cm $^{-1}$						
Signal-to-noise ratio: 500–2300						
Cell temperature: 300 \pm 0.5 K						
Average Doppler half-width γ^D : 0.013 cm $^{-1}$						

It was also possible to assign some lines in the $\nu_1 + 2\nu_2 + \nu_3 - \nu_2$ hot band.

The rotational energy levels of the second hexad are reported in Table 3. These new results are in good agreement with and improve upon our previous results (3, 4), as far as the accuracy and the coverage are concerned. The wavenumbers of the observed lines are listed in Table 4 along with their measured intensities, which are discussed in the next section.

3. Line intensities

We have already described the procedure used to derive precise, absolute $H_2^{16}O$ line intensities (10). There are two main sources of difficulties: first, the necessity to accurately check the total pressure of H_2O in natural spectra, and to recalibrate the absolute concentrations of $H_2^{16}O$ in the ^{18}O - and ^{17}O -enriched samples; second, the determination of the residual absorption due to traces of atmospheric water along the optical path. These two problems have been solved as explained in ref. 10, thus allowing us to perform reliable intensity measurements.

3.1. Measurement of line intensities by the curve-of-growth method: discussion of the results

The curve of growth of the equivalent-width method was used under the conditions described in ref. 11. In this way, the intensities of all the well-isolated lines were measured, with an average uncertainty of 6%. These values are listed in Table 4.

Since 31 of these 500 intensities had already been measured by other authors (6, 7), comparisons have been made between their results and ours (Table 5). For each line, the ratio R of the two available intensities has been calculated, and we find an average value $\bar{R} = 1.03 \pm 0.08$, which denotes a negligible systematic shift inside the stated uncertainties. Therefore, it appears that the consistency of these two independent sets of results is excellent, allowing us to ascertain that reliable absolute intensities have been obtained in the present work.

We have also listed in Table 5 the intensities introduced by Benedict in the atmospheric compilations (2). Although these previous values reproduce the relative line strengths well enough, large discrepancies appear with the measured absolute values, confirming the need of precise, individual line-intensity measurements to generate a reliable database.

3.2. Measurements of line intensities by the central-depth method

To complete the set of intensities obtained above, we have used a faster method (12). This method is based on the fact that the central depth $s(\sigma_0)$ of a line, observed under infinite

TABLE 2. Positions and intensities of the main $H_2^{16}O$ bands appearing between 7500 and 9500 cm $^{-1}$

Band	Band center (cm $^{-1}$)	Band intensity (10^{-22} cm $^{-1}$ /(molecule·cm $^{-1}$) at 296 K)
$5\nu_2$	7552.0 ^a	0.028 ^e
$4\nu_2 + \nu_3 - \nu_2$	8238.84 ^{cd}	0.059 ^c
$\nu_1 + 3\nu_2$	8273.9757 ^e	2.4 ^c
$3\nu_2 + \nu_3$	8373.8526 ^e	36 ^c
$\nu_1 + 2\nu_2 + \nu_3 - \nu_2$	8733.9846 ^e	0.41 ^c
$2\nu_1 + \nu_2$	8761.5820 ^e	3.6 ^c
$\nu_1 + \nu_2 + \nu_3$	8807.0003 ^e	498 ^c
$6\nu_2$	=8890	1.2 ^f
$\nu_2 + 2\nu_3$	9000.1365 ^e	12 ^c

^aValue calculated by Ulenikov and Ushakova (8).

^bMeasured value $\pm 20\%$ (this work), equal to the sum of the intensities of eight lines due to three resonating levels of (050).

^cValue from ref. 2.

^dAt room temperature, this weak hot band is not observable.

^eExperimental value (this work).

^fMeasured value $\pm 20\%$ (this work), equal to the sum of the intensities of seven lines due to the resonating level (060)(616).

resolution and centered at the wavenumber σ_0 , is related to its intensity S^0 (in cm $^{-2}$ ·atm $^{-1}$) by

$$[1] \quad A(\sigma_0) = 1 - \exp \left\{ - \left(S^0 x P l / \gamma^D \right) (\log 2/\pi)^{1/2} k[0, (\log 2)^{1/2} \gamma^L / \gamma^D] \right\}$$

where $k(0,y)$ is the value of the reduced Voigt profile at the center of the line (see Table 1 for the other notations). For the low pressures that we are concerned with, the variation of the term between the braces from one line to another is mainly due to the variations of S^0 and γ^D , which is proportional to σ_0 ; thus,

$$[2] \quad A(\sigma_0) = 1 - \exp \left\{ - \left(S^0 \alpha / \sigma_0 \right) \right\}$$

α being a constant. This is equivalent to

$$[3] \quad \alpha = -(\sigma_0 / S^0) \log [1 - A(\sigma_0)]$$

For each recorded spectrum, an average value of the coefficient α is determined from the available experimental results, i.e., the line intensities previously obtained by the curve-of-growth method and the corresponding line depths. Then, for this spectrum, the average value of α is used to derive the intensities of the other lines from their measured depths.

TABLE 5. Comparison of the line intensities measured in this work with those of other authors (intensities have been converted to $10^{-5} \text{ cm}^{-2} \cdot \text{atm}^{-1}$ at 300 K)

Line center (cm $^{-1}$) (this work)	Intensity calculated by Benedict (refs. 1, 2)	S_1^0 Measured intensity $\pm 6\%$ (this work)	S_2^0 Measured intensity $\pm 10\%$ (see refs. 6 and 7)	$R = S_1^0/S_2^0$ ($\bar{R} = 1.030 \pm 0.078$)
9207.8654	35.4	11.8	{ 11.8 ^a 12.3 ^b	1.000
9219.8520	14.4	3.85	3.53 ^c	0.959
9221.8855	3.87	2.16	2.02 ^c	1.069
9224.2465	5.53	3.13	2.82 ^c	1.110
9227.6952	13.0	4.93	4.82 ^c	1.023
9229.2923	40.3	14.6	12.8 ^c	1.141
9237.7975	1.17	0.661	0.696 ^c	0.950
9241.6079	1.32	0.783	0.689 ^c	1.136
9242.8597	0.874	0.443	0.500 ^c	0.886
9243.0742	6.11	1.67	1.60 ^c	1.044
9251.2391	2.74	2.00	2.01 ^c	0.995
9253.5825	7.09	2.74	2.69 ^c	1.019
9260.9181	2.01	1.53	1.48 ^c	1.034
9263.4351	2.40	1.30	1.31 ^c	0.992
9272.2582	1.88	1.27	1.21 ^c	1.050
9274.6482	2.30	1.49	1.50 ^c	0.993
9280.0388	10.2	3.80	3.90 ^c	0.974
9280.8167	18.8	7.20	8.27 ^c	0.871
9281.0825	6.31	2.51	2.38 ^c	1.055
9283.5661	8.40	1.06	1.04 ^c	1.019
9289.8957		1.14	1.05 ^c	1.086
9303.1347	2.82	1.28	1.30 ^c	0.985
9304.3962	8.81	3.92	3.94 ^c	0.995
9305.4429	18.9	5.97	6.35 ^c	0.940
9319.8980	3.40	0.963	1.08 ^c	0.892
9323.1833	3.21	1.80	1.82 ^c	0.989
9327.4567	1.22	0.669	0.586 ^c	1.142
9328.9881	3.63	0.796	0.785 ^c	1.014
9350.3986	5.63	1.83	1.61 ^c	1.137
9351.1494	1.40	0.781	0.730 ^c	1.070
9366.5925	0.434	0.880	0.778 ^c	1.131
9371.7630	2.35	0.714	0.597 ^c	1.196

^aValue obtained by Brault *et al.* (6) from a measurement performed at 296 K.

^bValue obtained by Brault *et al.* (6) from a measurement performed at 297 K.

^cValue measured by Cherepanov *et al.* (7).

To assess the validity of such a method, we have made several tests (12).

(i) Equation (1) is valid only for infinite resolution, but taking into account the range of values of γ^D , γ^L , and the resolution limit, we have checked that it was always possible to use an effective constant α with very good accuracy (standard deviations from 2 to 4.5% depending on the spectrum). In particular, it should be noted that we did not detect any systematic deviation related to either the line depth or the wavenumber.

(ii) From (1), α can be related to known quantities

$$(4) \quad \alpha = \beta(\sigma_0 x^P I / \gamma^D) (\log 2/\pi)^{1/2} k(0, (\log 2)^{1/2} \gamma^L / \gamma^D)$$

the constant β (slightly less than unity) being introduced to take into account the effect of the apparatus function. For similar resolutions, the value of β should not depend upon the quantities appearing in (4). We have checked that this is true for a wide variety of spectra, since we find the value of β to be remarkably constant: $\beta = 0.96 \pm 0.02$.

(iii) As already mentioned, several precautions have to be taken to measure the H₂¹⁶O line intensities, especially because of traces of atmospheric water vapor along the optical path.

Indeed, intensity measurements of very strong lines need low optical-thickness spectra, where the atmospheric absorption is not negligible. Then, the atmospheric Lorentzian part of the absorption profile may become important so that (1), which describes the absorption caused by just the gas being present in the cell, is no longer valid. In fact, using as tests similar spectra of the second triad of H₂¹⁶O for which an extensive set of accurately calculated intensities is available (13), we have found that the method could still be used for the range of line depth and optical-thickness values we encountered in this work. (However, once the Lorentzian contribution has been removed, we have effectively found the same value of β that was mentioned above. This is additional proof of the significance of the method.)

(iv) Finally, the comparison of the deduced intensity values for the same line, from various records, shows a good agreement.

To conclude, this method appears to be significant and easy to use. The uncertainty in the obtained intensities is mainly due to the uncertainty in the depth of the lines concerned, which are all, more or less, perturbed by neighbouring lines (this is why the equivalent-width method could not be used for these lines).

These intensities are listed in Table 4. The reported uncertainties are estimated as follows. For "good" lines, the uncertainty can be between 6 and 15%, and a mean value 10% is mentioned. For perturbed lines, the uncertainty is in the range 15–25%, and a mean value of 20% is given. For strong overlappings, a mean uncertainty of 50% is given. (When blending occurs, only the total intensity can be measured and this is repeated for each line located at the same wavenumber; in this case, the stated uncertainty concerns the whole intensity, and is not the uncertainty of each blended line.)

4. Conclusions

Using Fourier-transform spectra of water between 8000 and 9500 cm^{-1} , we have obtained an extensive set of accurate rotational energy levels for the second hexad of interacting states of H_2^{16}O . We have measured the intensities of all the observable lines; their uncertainty varies from 6 to 50%, depending upon the line, with a mean value of 10%. This extensive set of line positions and intensities gives a quasi-complete picture of the absorption of H_2^{16}O at room temperature in the studied spectral region.

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H₂¹⁶O: Line positions and intensities between 9500 and 11500 cm⁻¹. The interacting vibrational states (041), (220), (121), (022), (300), (201), (102), and (003)

J.-P. CHEVILLARD, J.-Y. MANDIN, J.-M. FLAUD, AND C. CAMY-PEYRET

Laboratoire de Physique Moléculaire et Atmosphérique,
Université Pierre-et-Marie-Curie et Centre National de la Recherche
Scientifique (CNRS),
Tour 13, 4, place Jussieu,
75252 Paris CEDEX 05, France

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Résumé

Des spectres par transformée de Fourier de la vapeur d'eau (résolution: 0.015 cm^{-1}) ont été analysés entre 9500 et 11500 cm^{-1} . Les valeurs précises de 557 niveaux d'énergie rotationnels appartenant aux états vibrationnels interagissants (041), (220), (121), (022), (300), (201), (102), et (003) de la première décade d' H_2^{16}O , ont été déterminées. De plus, on a mesuré avec précision les intensités de 718 raies (incertitude: 7%). Dans le but d'augmenter le nombre d'intensités expérimentales (nécessaires pour les applications atmosphériques), une méthode plus rapide utilisant les profondeurs mesurées des raies, a permis d'obtenir 1695 intensités supplémentaires, avec une incertitude moyenne d'environ 15% .

Abstract

Water vapor Fourier-transform spectra (resolution: 0.015 cm^{-1}) have been analyzed between 9500 and 11500 cm^{-1} . Accurate values of 557 rotational energy levels, belonging to the interacting vibrational states (041), (220), (121), (022), (300), (201), (102), and (003) of the first decad of H_2^{16}O , have been determined. Moreover, 718 line intensities have been accurately measured (uncertainty: 7%). In order to increase the number of experimental intensities (needed by atmospheric applications), a faster method, using the measured line depths, has led to the obtention of 1695 additional intensities, with an average uncertainty of about 15%.

1. Introduction

This paper is the continuation of our previous works about the water molecule (1,2), the absorption of which plays a major role in atmospheric applications or in radiative transfer studies. After the analysis of the $H_2^{16}O$ spectrum between 8000 and 9500 cm^{-1} (1), we present here the 9500- to 11500 cm^{-1} spectral region for the same molecule. This region was first studied by Benedict (3) working on the solar spectra of Delbouille and Roland (3) (resolution: between 0.10 and 0.05 cm^{-1} depending upon the wavelength); later on, these results were introduced in the atmospheric compilation (4), with some modifications.

We had already studied this spectral region, but for the $H_2^{18}O$ isotopic species (2). So, in order to have a more complete picture of the water vapor absorption in this region and to improve the accuracy of the previous results, we have studied several spectra (resolution: 0.015 cm^{-1}) recorded with the Fourier-transform spectrometer built by Brault (5). The analysis of these spectra has led to the determination of 557 accurate rotational energy levels for the interacting vibrational states (041), (220), (121), (022), (300), (201), (102), and (003), which belong to the first decad of H_2O .

In the spectral region we dealt with, the knowledge of experimental intensities is very incomplete. The atmospheric data base (4) gives some values, but they were obtained by Benedict from the equivalent widths measured in solar spectra, so, most of them are known with large uncertainties. Latter on, Giver et al. (6) measured accurate intensities for 97 lines between 10400 and 10750 cm^{-1} . To extend this set of data, we used the equivalent width method to measure 718 intensities of well isolated lines (uncertainty: 7%). Besides, in order to provide a complete list of reliable individual line intensities, we used the faster central depth method already described (1), to obtain the intensities of all the remaining lines: thus, 1695 additional intensities have been measured with an average uncertainty of about 15% .

2. Experimental details and analysis

The experimental details and the data reduction procedure have already been discussed (1,2,) so, we give here only the details relevant to the present study. The ^{18}O -enriched, ^{17}O -enriched, and natural water vapor spectra were recorded at the National Solar Observatory (Kitt Peak, AZ), with the Brault's Fourier-transform apparatus (5). The experimental conditions and the characteristics of these spectra are gathered in Table 1. Figure 1 is a representative portion of the spectrum which shows clearly the quality of the signal-to-noise-ratio.

As already said in the case of H_2^{18}O (2), 10 resonating vibrational states are involved in the studied spectral region: they form the so-called first decad of the water molecule, i.e., the polyad of interacting states $\{(060), (140), (041), (220), (121), (022), (300), (201), (102), (003)\}$. Among the 10 corresponding cold bands, the $\nu_1+4\nu_2$ band is so weak that it could not be observed, even in our long absorption path spectra. Also, it is interesting to notice that, owing to a few resonant levels, we could observe the very weak $2\nu_2+2\nu_3$ band, whereas it was unobservable for H_2^{18}O (2), because the optical thickness of H_2^{18}O was too small. Let us recall also that the $6\nu_2$ band absorbs around 8600 cm^{-1} , and is visible only through the resonating level (060)[616] (1,7). On the whole, the 8 following bands were analyzed: $4\nu_2+\nu_3$, $2\nu_1+2\nu_2$, $\nu_1+2\nu_2+\nu_3$, $2\nu_2+2\nu_3$, $3\nu_1$, $2\nu_1+\nu_3$, $\nu_1+2\nu_3$, and $3\nu_3$.

Accurate energy values were known only for a few levels of the (121) vibrational state, from some lines of the $\nu_1+2\nu_2+\nu_3-\nu_2$ hot band observed in the 8000- to 9500 cm^{-1} region (1). Nevertheless, a good starting point for the analysis of the spectra was provided by the energy levels of Benedict (3); and, except for a few cases, our values confirm and improve the energy levels that Benedict primarily observed or predicted, despite the low resolution of the spectra he had at his disposal.

The resonances are numerous, some of them involving simultaneously more than two levels. In particular, almost half of the very close (300) and (201)

rotational levels interact with each other, or with levels of other vibrational states. A typical example is given by the levels (201)[808] at $11317.2662\text{ cm}^{-1}$, and (121)[826] at $11322.4512\text{ cm}^{-1}$. We had already pointed out this resonance in the case of H_2^{18}O (2), and it is particularly interesting to note the differences that appear between the two isotopic molecules H_2^{16}O and H_2^{18}O . As one can see on Fig. 2, the relative positions of the resonant levels are different for the two molecules: for H_2^{16}O , (201)[808] is about 5.2 cm^{-1} below (121)[826], whereas it is only about 3.6 cm^{-1} above for H_2^{18}O . This means a stronger interaction for H_2^{18}O than for H_2^{16}O . Indeed, the two levels (201)[808] and (201)[818], which should be quasi-degenerated in the unperturbed scheme because they form a doublet, are actually well separated, i.e., by about 1.2 cm^{-1} for H_2^{16}O , but only by 0.6 cm^{-1} for H_2^{18}O . Furthermore, as (121)[826] is above (201)[808] for H_2^{16}O , this level is shifted downwards with respect to (201)[818], whereas it is shifted upwards for H_2^{18}O . Such differences in the positions of the levels give rise to different spectra: see Fig. 1, which should be compared with Fig. 1 of ref. 2. This discussion shows that the effect of the interactions cannot be simply transposed from one isotope to another (see also ref. 8).

Another interesting example of strong difference between the spectra of the two isotopes concerns the K_c doublet-levels (121)[909] and (121)[919], which are separated by more than 1.8 cm^{-1} for H_2^{16}O , but which are very close to each other for H_2^{18}O . This is because of a strong Fermi-interaction between the levels (121)[919] and (041)[937] of H_2^{16}O , whereas this resonance does not exist in the case of the H_2^{18}O molecule (see Table 3 of ref. 2): indeed, the level (041)[937] of H_2^{18}O is located so that no strong interaction occurs, and it cannot be observed for this reason. Such a fact is not surprising since the structure of the rotational levels of the (041) vibrational state is subject to a noticeable change with the isotopic substitution, because of the large value of the v_2 -quantum number.

A comment can be made about the [000] rotational levels which, of course, are obtained by only one transition. Though this transition generally gives rise to a weak line, it can be easily identified using sum rules (9,10). For example, the following relation gives an approximate value of the energy $E[000]$ without any diagonalization of the hamiltonian matrix:

$$[1] \quad E|000\rangle = (9/5) E|101\rangle + \{ E|221\rangle - E|202\rangle - E|220\rangle \} + \dots \\ \dots + (1/5) \{ E|303\rangle + E|321\rangle - E|322\rangle \}.$$

This very simple formula is interesting. First, it only needs to know the energy of 7 levels. And second, when these levels are non resonant, it provides a very good approximation of $E|000\rangle$: indeed, the predicted value is correct (10) within an error of 144 times the H_J constant of the Watson-Hamiltonian (11,12) and with an uncertainty of 5.4 times the mean uncertainty on the experimental energy levels; this leads to an overall error on the estimation of the $E|000\rangle$ of about 3×10^{-3} cm $^{-1}$. This formula allowed to search the corresponding line and to find it without ambiguity. This is even possible when some of the levels involved in [1] are resonant, [as for the (220) and (201) states].

A similar problem of assignment arises for some doublet-levels of high J -value with K_a equal 0 or 1. Usually, these levels are obtained from only one doublet-line but, since such lines appear as series (12,10), it is rather easy to perform the assignment. Furthermore, they are recognizable in N_2 -broadened spectra (not mentioned in Table 1), since this type of transitions give rise to very narrow lines, as it was already observed between 8500 and 9500 cm $^{-1}$ (15). (The measurement of N_2 -broadening coefficients of lines between 9500 and 11500 cm $^{-1}$ is in progress.)

3. Results

3.1. Line positions and energy levels

The experimental positions of the 2413 assigned lines, between 9500 and 11500 cm^{-1} , are listed in Table 2. From them, 557 rotational energy levels have been determined. These energy levels are reported in Table 3, together with their uncertainty and with the number of observed transitions involving each level.

The absolute wavenumbers of Tables 2 and 3 have been obtained through a careful calibration procedure (10,14), and their comparison with previous values (3) deserves some discussion. First, it is important to recall that the results of Benedict (3), which have been reported in the 1986 HITRAN data base (4), come from solar spectra and are therefore air-shifted wavenumbers. The few experimental values of air-shift coefficients of H_2O lines which have been published (see, e.g., refs. 6,16,17, and references therein), show that this air-shift is not negligible since it ranges between -3×10^{-3} and -40×10^{-3} $\text{cm}^{-1} \cdot \text{atm}^{-1}$. Thus, the HITRAN wavenumbers for the concerned spectral regions can be underestimated by a similar amount. In fact, we have noted that the HITRAN wavenumbers are on the average lower than ours, which are free from air-shift since they are measured on pure H_2O spectra. The self-shift could play a role but, although only two measured values of the self-shift have been published (18,19) to our knowledge, one can reasonably think that this shift is negligible in our spectra, because of their low H_2O pressure (see Table 1).

For the same reason, we have also observed a discrepancy between the wavenumbers of refs. 20,21 and those of the HITRAN data base. Such differences could have troublesome consequences, especially for lidar applications. To cope with this problem, N_2 -shift measurements are in progress (10), using some other spectra we had recorded at the National Solar Observatory, with half an atmosphere of N_2 .

3.2. Line intensities

Using the curve of growth method, we have measured the intensities of 718 well isolated lines. They are reported in Table 2 and their average uncertainty is 6% (as far as absolute values of intensities are concerned, the uncertainty to take into account is 7% : see refs. 14, 22, 23).

Since 53 of these intensities had already been measured by Giver et al. (6) (resolution: 0.045 cm^{-1} , and average uncertainty: 3.3% for the concerned lines), comparisons were made between their results and ours (see Table 4). The average ratio of the two intensities is: $\bar{R} = 0.960 \pm 0.077$; this good agreement proves the consistency of these two independant sets of results.

To complete the list of intensities obtained above, we have used the central depth method detailed in ref. 1. The additional intensities thus measured are listed in Table 2. For not too perturbed lines, the uncertainty lies between 6 and 15%. For perturbed lines, the uncertainty ranges from 15 to 25%, and a value of 20% is given. For strong overlappings, or for very weak lines, the uncertainty can be more important and a mean value 50% is reported. When close blendings occur, only the total intensity can be measured and is repeated for each line located at the same wavenumber.

Since we wanted to make precise comparisons between the intensities measured by different authors, Table 4 contains only our most accurate intensities, i.e., those having a 6% uncertainty. But it is interesting to notice that the comparison of the intensities of 41 other less precise lines, that we obtained by the central depth method, with the corresponding intensities of Giver et al. (6) gives rise to the same value of the average ratio \bar{R} . This shows again the coherence of the method and of its results.

4. Conclusion

Using water vapor Fourier-transform spectra recorded between 9500 and 11500 cm⁻¹, we have obtained an extensive set of accurate rotational energy levels for eight interacting vibrational states belonging to the first decad of H₂¹⁶O. We have measured the intensities of all the observable lines, their uncertainty ranging from 6 to 50% depending upon the line, with an average value of 15%. This extensive set of line positions and intensities greatly improve upon the previous results, as far as the accuracy and the coverage are concerned.

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FIG. 1. Portion of a ^{17}O -enriched spectrum used in this work. The plotted spectrum is a part of the spectrum number 5 (see Table 1), which has been apodized. The lines marked with a triangle are due to H_2^{16}O (see Table 2). Those marked with a black circle are due to H_2^{18}O (see ref. 2). The line marked with a diamond belongs to H_2^{17}O . The H_2^{16}O transitions, the assignment of which is mentioned, illustrate the strong Fermi-resonance between the levels (121)[826] and (201)[808]. This interaction has the same qualitative effects as for H_2^{18}O (see Fig. 1 of ref. 2), except that the relative line positions are reversed, because of the differences in the structure of the H_2^{16}O and H_2^{18}O levels (see Fig. 2).

FIG. 2. Comparison of the relative positions of the energy levels of $H_2^{16}O$ and $H_2^{18}O$, in the case of the Fermi-resonance between (121)|826| and (201)|808|. The level (201)|818| is not perturbed. The approximate position of the level (201)|808| in the absence of interaction is indicated by dots. The mentioned energies are in cm^{-1} . (See Sect. 2 for discussion.)

TABLE 1. Experimental conditions and characteristics of the absorption spectra
(1 atm = 1013 hPa). Common characteristics: studied spectral region, 9500–11500
 cm^{-1} ; signal-to-noise ratio, 500–1000; cell temperature, 300 ± 0.5 K; average
Doppler half-width, 0.015 cm^{-1} .

TABLE 2. List of experimental line positions and intensities for the bands of H_2^{16}O observed between 9500 and 11500 cm^{-1} at 300 K

NOTES: SIGMA: observed position of the line in cm^{-1} . P: the line is perturbed by neighbouring lines or by the noise. B: the line is blended with another line (of H_2^{16}O or of another isotope); however, a line blended with another one stronger by a factor larger than 10 is not mentioned; note that, when a blending occurs, the total measured intensity is repeated for each line blended at the same wavenumber. An asterisk indicates a poor quality line which has not been used in the calculation of the energy levels. VIB: vibrational quantum numbers v_1' , v_2' , v_3' of the upper level. The lower vibrational level is the fundamental (000). J' KA' KC' J" KA" KC": rotational quantum numbers of the upper and lower levels respectively. E": energy of the lower level in cm^{-1} . INTENSITY: measured line intensity at 300 K expressed in $\text{cm}^{-2}\text{atm}^{-1}$. % : uncertainty in the measured intensity (see text, Sect. 3.2).

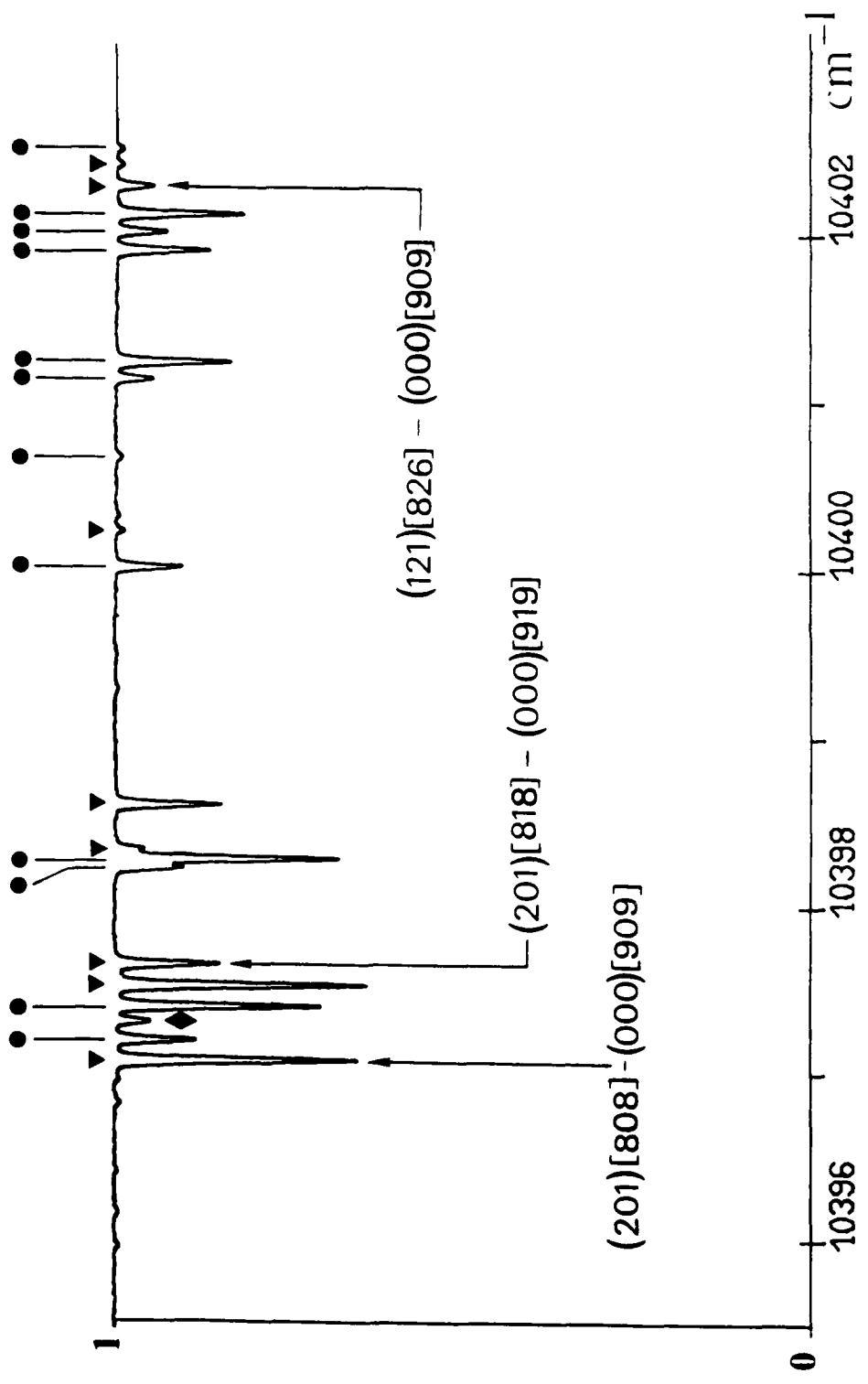
TABLE 3. Experimental rotational energy levels for the observed vibrational states of the first decad of $H_2^{16}O$

NOTES: E: experimental energy in cm^{-1} . DELTA.E: uncertainty in the energy value, equal to one standard deviation in units of 10^{-3} cm^{-1} . N: number of observed lines arriving at the corresponding level. Let us recall that the resonant level (060)[616] at $9400.6413 \text{ cm}^{-1} \pm 0.41 \times 10^{-3} \text{ cm}^{-1}$, has been observed by 7 lines in the second hexad region (1,7).

TABLE 4. Comparison of line intensities measured in this work with those of Giver et. al. (6)

NOTES: SIGMA: line center in cm^{-1} , from this work. S01: intensity measured by Giver et. al. (6), converted to $\text{cm}^{-2}\text{.atm}^{-1}$ at 300 K (average uncertainty: 3.3% ; but, as far as absolute intensities are concerned, this uncertainty should be slightly increased: see ref. 15). S02: intensity measured in this work (uncertainty: 7%). R: ratio S02/S01, with $\bar{R} = 0.960 \pm 0.077$ for the 53 lines. See Table 2 for the other notations.

FIG. 4 *Can. J. Phys.* *J.-P. CHENILLEAU ET AL.*



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FIG. 2 Com. J. Phys.

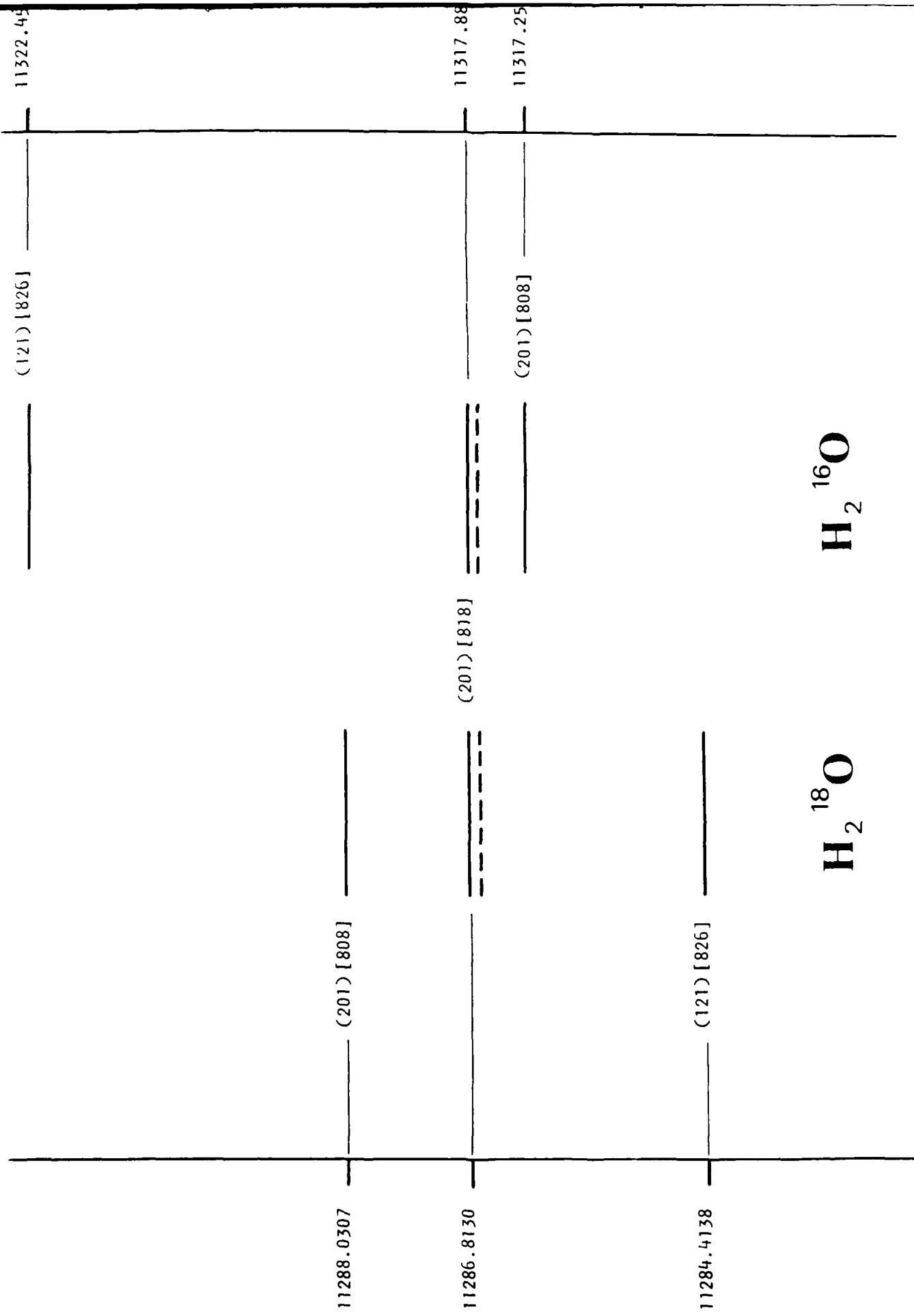


TABLE I
Can. J. Phys.

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Type of spectrum	Spectrum number	Unapodized	Total pressure	Average	H_2	H_2	H_2
		resolution (10^{-3} cm^{-1})	$P \pm 1\%$ (10^{-3} atm)	Lorentz half-width (10^{-3} cm^{-1})	Absorption path ℓ (cm)	Concentration x $P \ell$ (cm, atm)	Optical thickness
Natural							
1	17	1.97	0.7	4.3	396	0.997	85.2
2	17	22.8	8.0	4.3	396	0.997	986
^{18}O enriched							
3	13	3.68	1.3	4	900	0.27 ± 0.01	4.87
4	13	3.58	1.3	4.3	396	0.27 ± 0.01	42.0
^7O enriched							
5	13	6.25	2.2	4	900	0.79 ± 0.03	24.2
6	13	6.25	2.2	4.3	396	0.79 ± 0.03	214

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J HA RC	0 4 F			2 2 0			1 2 1			0 2 2			3 0 0			2 0 1			1 0 2			0 0 3				
	E DELIA EN	CM -1	10-3CM -1	E DELIA EN	CM -1	10-3CM -1	E DELIA EN	CM -1	10-3CM -1	E DELIA EN	CM -1	10-3CM -1	E DELIA EN	CM -1	10-3CM -1	E DELIA EN	CM -1	10-3CM -1	E DELIA EN	CM -1	10-3CM -1	E DELIA EN	CM -1	10-3CM -1		
0 0 0	933 585	0 9 1	10284 3670	2 9 1	10128 7109	0 9 1	10599 6663	8 8 1	10613 3547	2 9 1	10688 8757	0 9 1	11032 4056	0 9 1	11032 4056	0 9 1	11032 4056	0 9 1	11032 4056	0 9 1	11032 4056	0 9 1	11032 4056	0 9 1	11032 4056	0 9 1
1 0 1	937 1976	0 8 2	10307 4477	0 8 2	10151 9300	0 5 3	10622 4172	0 6 2	10636 5007	0 5 3	10891 6758	0 6 2	11055 4716	0 6 2	11055 4716	0 6 2	11055 4716	0 6 2	11055 4716	0 6 2	11055 4716	0 6 2	11055 4716	0 6 2	11055 4716	0 6 2
1 1 0	938 6929	0 8 2	10124 8053	0 8 3	10189 1162	0 8 2	10833 5548	0 5 3	10847 4185	0 8 2	10902 5280	0 5 3	11055 7745	0 6 2	11055 7745	0 6 2	11055 7745	0 6 2	11055 7745	0 6 2	11055 7745	0 6 2	11055 7745	0 6 2	11055 7745	0 6 2
1 1 0	9395 3296	0 8 2	10330 7309	0 9 2	10375 5942	0 8 2	10839 6073	0 6 2	10852 6074	0 6 2	10908 1348	0 6 2	11071 1125	0 6 2	11071 1125	0 6 2	11071 1125	0 6 2	11071 1125	0 6 2	11071 1125	0 6 2	11071 1125	0 6 2	11071 1125	0 6 2
2 0 2	963 4914	0 8 3	10352 4226	0 8 2	10197 2151	0 4 4	10666 4779	0 5 4	10680 5447	0 5 4	10935 8203	0 6 2	11099 9735	0 4 4	11099 9735	0 4 4	11099 9735	0 4 4	11099 9735	0 4 4	11099 9735	0 4 4	11099 9735	0 4 4	11099 9735	0 4 4
2 1 1	939 7127	0 9 3	10182 1791	0 5 3	10410 2116	0 5 4	10673 8774	0 5 4	10687 8293	0 5 4	10943 3235	0 4 4	11106 5829	0 5 4	11106 5829	0 5 4	11106 5829	0 5 4	11106 5829	0 5 4	11106 5829	0 5 4	11106 5829	0 5 4	11106 5829	0 5 4
2 2 1	939 0786	0 9 2	10182 8491	0 5 3	10427 8863	0 4 4	10689 8175	0 5 3	10703 0830	0 5 4	10958 9189	0 6 3	11122 5870	0 5 3	11122 5870	0 5 3	11122 5870	0 5 3	11122 5870	0 5 3	11122 5870	0 5 3	11122 5870	0 5 3	11122 5870	0 5 3
2 2 1	10039 4198	0 8 2	10439 0981	0 5 3	10480 3229	0 5 3	10670 6328	0 6 3	10724 2081	0 4 4	10731 0132	0 5 3	10922 4537	0 4 4	11153 2711	0 5 3	11153 2711	0 5 3	11153 2711	0 5 3	11153 2711	0 5 3	11153 2711	0 5 3	11153 2711	0 5 3
2 2 0	10040 3024	0 8 2	10440 1058	0 6 2	10481 5346	0 4 4	10725 4831	0 5 4	10738 4316	0 4 4	10953 8806	0 5 4	11154 8633	0 4 4	11154 8633	0 4 4	11154 8633	0 4 4	11154 8633	0 4 4	11154 8633	0 4 4	11154 8633	0 4 4	11154 8633	0 4 4
3 0 3	9310 2522	0 8 4	10417 2210	0 5 2	10462 2196	0 5 4	10655 8136	0 5 3	10729 5223	0 5 3	10742 6213	0 5 4	10939 0217	0 6 3	11183 4767	0 4 5	11183 4767	0 4 5	11183 4767	0 4 5	11183 4767	0 4 5	11183 4767	0 4 5	11183 4767	0 4 5
3 1 2	9390 3595	0 9 3	10423 1239	0 8 4	10470 3451	0 5 4	10659 7731	0 6 3	10764 3479	0 5 4	10777 5587	0 4 5	11033 0803	0 5 4	11166 8637	0 4 5	11166 8637	0 4 5	11166 8637	0 4 5	11166 8637	0 4 5	11166 8637	0 4 5	11166 8637	0 4 5
3 2 2	10268 8170	0 8 3	10460 0561	0 5 4	10504 0554	0 5 3	10638 7731	0 6 3	10792 7022	0 9 2	10805 0243	0 4 5	11080 8477	0 5 5	11229 5388	0 4 5	11229 5388	0 4 5	11229 5388	0 4 5	11229 5388	0 4 5	11229 5388	0 4 5	11229 5388	0 4 5
3 2 1	10110 5405	0 9 5	10509 5368	0 6 4	10555 7245	0 5 4	10798 5272	0 4 5	10811 4833	0 5 5	10967 3460	0 4 5	11131 4623	0 5 5	11331 5522	0 4 5	11331 5522	0 4 5	11331 5522	0 4 5	11331 5522	0 4 5	11331 5522	0 4 5		
3 3 1	10114 2488	0 9 5	10513 7465	0 5 4	10650 0329	0 5 4	10850 2355	0 5 4	10862 6729	0 5 5	10874 7717	0 5 5	11074 4715	0 4 5	11244 4715	0 4 5	11244 4715	0 4 5	11244 4715	0 4 5	11244 4715	0 4 5	11244 4715	0 4 5		
3 3 0	10235 8206	0 8 3	10612 2455	0 5 4	10812 3870	0 5 4	10850 2233	0 5 3	10879 6024	0 5 4	10924 1241	0 3 7	11079 6537	0 5 3	11244 4715	0 4 5	11244 4715	0 4 5	11244 4715	0 4 5	11244 4715	0 4 5	11244 4715	0 4 5		
4 0 4	10368 1878	0 5 4	10459 8744	0 5 4	10544 9918	0 4 5	10611 9039	0 5 4	10682 6593	0 4 5	10825 0286	0 4 5	11081 5245	0 4 5	11245 8962	0 4 5	11245 8962	0 4 5	11245 8962	0 4 5	11245 8962	0 4 5	11245 8962	0 4 5		
4 1 4	10701 3985	0 8 6	10516 0329	0 8 4	10549 4009	0 5 5	10742 8614	0 6 4	10874 0187	0 4 5	11061 6880	0 6 5	11261 5230	0 5 4	11296 7457	0 4 5	11296 7457	0 4 5	11296 7457	0 4 5	11296 7457	0 4 5	11296 7457	0 4 5		
4 2 3	10133 8604	0 9 5	10581 0314	0 9 3	10607 6732	0 4 6	10883 2259	0 4 5	10984 5359	0 4 5	11094 0286	0 4 5	11261 7835	0 4 5	11331 4623	0 5 5	11331 4623	0 5 5	11331 4623	0 5 5	11331 4623	0 5 5	11331 4623	0 5 5		
4 2 2	10204 4914	0 9 5	10594 5398	0 5 4	10641 8897	0 5 5	10857 1116	0 4 5	10911 1012	0 5 4	10989 9734	0 4 7	11126 0867	0 4 5	11328 1378	0 4 5	11328 1378	0 4 5	11328 1378	0 4 5	11328 1378	0 4 5	11328 1378	0 4 5		
4 2 1	10218 4820	0 5 4	10614 4010	0 5 4	10745 1395	0 4 6	10746 1675	0 4 5	10957 4221	0 5 4	10989 1188	0 4 6	11224 6298	0 4 5	11384 1581	0 5 5	11384 1581	0 5 5	11384 1581	0 5 5	11384 1581	0 5 5	11384 1581	0 5 5		
4 3 1	10312 5892	0 5 3	10348 3018	0 5 2	10483 8745	0 5 4	10877 3449	0 3 9	11061 2735	0 5 4	11048 3833	0 5 6	11050 2852	0 3 1	11314 9939	0 4 5	11687 5225	0 5 4	11687 5225	0 5 4	11687 5225	0 5 4	11687 5225	0 5 4		
4 3 0	10359 5387	0 9 4	10493 5446	0 9 2	10645 4278	0 4 5	10877 3695	0 5 4	11061 2992	0 6 3	11048 4128	0 9 3	11060 3339	0 5 4	11347 8633	0 5 5	11771 1518	0 8 5	11771 1518	0 8 5	11771 1518	0 8 5	11771 1518	0 8 5		
5 0 5	10150 5540	0 5 2	10599 2394	2 8 3	10844 8204	0 6 3	10844 3670	0 5 4	10922 3656	0 5 4	10922 3656	0 5 4	11177 1874	0 4 5	11345 6246	0 4 5	11345 6246	0 4 5	11345 6246	0 4 5	11345 6246	0 4 5	11345 6246	0 4 5		
5 1 5	10159 0593	0 8 3	10601 2666	0 8 4	10846 7008	0 4 5	10875 3404	0 5 5	10986 0466	0 5 3	11026 3154	0 4 6	11244 9985	0 4 5	11414 7949	0 4 5	11414 7949	0 4 5	11414 7949	0 4 5	11414 7949	0 4 5	11414 7949	0 4 5		
5 2 4	10202 1832	0 8 3	10512 1195	2 8 2	10154 1530	0 4 5	10888 9863	0 4 5	11023 3986	0 4 5	11023 3986	0 4 5	11293 2966	0 4 6	11459 2118	0 5 5	11459 2118	0 5 5	11459 2118	0 5 5	11459 2118	0 5 5	11459 2118	0 5 5		
5 2 3	10320 5893	0 4 4	10348 3018	0 5 2	10742 0499	0 4 5	10785 8543	0 5 5	11023 4394	0 4 5	11083 3959	0 4 7	11336 7147	0 4 7	11500 4476	0 4 6	11500 4476	0 4 6	11500 4476	0 4 6	11500 4476	0 4 6	11500 4476	0 4 6		
5 2 2	10336 5002	0 9 5	10443 4278	0 4 5	10824 9746	0 5 4	10867 7489	0 5 5	11077 6701	0 5 5	11078 3668	0 4 5	11307 5224	0 4 5	11687 6357	0 5 4	11687 6357	0 5 4	11687 6357	0 5 4	11687 6357	0 5 4	11687 6357	0 5 4		
5 1 5	10611 1033	0 8 3	10611 2899	1 7 4	10696 3088	0 4 5	11182 2168	0 5 5	11185 4854	0 5 5	11177 1315	0 4 7	11422 3753	0 3 7	11693 6430	0 6 3	11693 6430	0 6 3	11693 6430	0 6 3	11693 6430	0 6 3	11693 6430	0 6 3		
5 1 4	10641 0557	0 6 3	10715 4348	0 6 3	10716 3092	0 6 4	10762 0462	0 5 5	10872 3522	0 5 5	11144 5054	0 4 5	11307 4058	0 5 5	11573 0822	0 5 5	11573 0822	0 5 5	11573 0822	0 5 5	11573 0822	0 5 5	11573 0822	0 5 5		
5 1 3	10626 1346	0 8 2	10452 5741	0 8 3	10648 0628	0 8 3	10888 3118	0 5 6	10939 5481	0 4 5	11221 5013	0 4 5	11476 6334	0 4 6	11686 4954	0 4 6	11686 4954	0 4 6	11686 4954	0 4 6	11686 4954	0 4 6	11686 4954	0 4 6		
5 1 2	10627 0266	0 5 4	10627 0266	0 5 4	10627 0266	0 5 4	10627 0266	0 5 4	11126 2587	0 4 7	11137 0382	0 5 6	11573 9592	0 4 6	11771 1518	0 8 5	11771 1518	0 8 5	11771 1518	0 8 5	11771 1518	0 8 5	11771 1518	0 8 5		
5 1 1	10633 9772	0 8 6	10633 9772	0 8 6	10633 9772	0 8 6	10633 9772	0 8 6	11126 2721																	

J K A KC	0 4 1			2 2 0			1 2 1			0 2 2			3 0 0			2 0 1			1 0 2			0 0 3		
	DELIA E N CM-1 10-3CM-1			DELIA E N CM-1 10-3CM-1			DELIA E N CM-1 10-3CM-1			DELIA E N CM-1 10-3CM-1			DELIA E N CM-1 10-3CM-1			DELIA E N CM-1 10-3CM-1			DELIA E N CM-1 10-3CM-1			DELIA E N CM-1 10-3CM-1		
7 0 7	10418 1024	0 9 2	10848 4533	0 9 3	10894 4854	0 5 3	11154 2064	0 6 4	11150 5635	0 5 5	11424 3180	0 9 2	11590 5927	0 5 4	11424 5310	0 5 4	11590 5659	0 5 3	11424 5310	0 5 4	11590 5927	0 5 3		
7 1 7	10421 0437	0 5 2	10868 8862	0 9 3	10894 8230	0 5 3	11154 3953	0 5 4	11167 5652	0 4 5	11281 4897	0 4 5	11537 0894	0 4 5	11702 5937	0 5 5	11281 4897	0 4 5	11537 0894	0 4 5	11702 5937	0 5 5		
7 1 8	10522 2728	0 9 2	10985 8708	0 5 4	11031 8641	0 5 5	11266 9839	0 4 5	11286 6943	0 5 6	11283 1409	0 4 5	1150 4441	0 5 4	11706 2258	0 4 5	11286 6943	0 5 6	1150 4441	0 5 4	11706 2258	0 4 5		
7 2 8	10618 1248	0 6 4	10641 3204	0 4 6	11116 4957	0 5 5	11343 8223	0 4 6	11355 1994	0 4 6	11815 2241	0 4 6	11639 4141	0 5 6	11782 4734	0 4 6	11815 2241	0 4 6	11639 4141	0 5 6	11782 4734	0 4 6		
7 2 9	10685 3912	0 9 2	11131 0401	0 6 4	11361 0038	0 5 5	11372 5672	0 4 5	11381 2322	0 4 6	11639 4141	0 5 6	11803 3848	0 4 6	11639 4141	0 5 6	11803 3848	0 4 6	11639 4141	0 5 6	11803 3848	0 4 6		
7 3 4	11192 1280	0 5 5	11170 3190	0 4 7	11398 8558	0 5 5	11398 8558	0 5 5	11410 5687	0 4 8	11480 4987	0 4 8	11480 4987	0 4 8	11480 4987	0 4 8	11480 4987	0 4 8	11480 4987	0 4 8	11480 4987	0 4 8		
7 4 4	11308 8982	0 5 4	11499 4230	0 6 6	11485 4752	0 5 5	11470 1813	0 5 5	11474 0562	0 5 5	11474 0562	0 5 5	11742 8774	0 4 8	11904 2017	0 5 5	11742 8774	0 4 8	11904 2017	0 5 5	11742 8774	0 4 8		
7 4 5	11487 9120	0 4 5	11587 7205	0 7 6	11597 3435	0 4 7	11587 7205	0 7 6	11597 7081	0 5 5	11852 1635	0 5 7	12009 9005	0 5 4	11852 1635	0 5 7	12009 9005	0 5 4	11852 1635	0 5 7	12009 9005	0 5 4		
7 5 2	11682 3361	0 5 4	11739 1733	0 5 4	11739 1740	0 4 7	11739 1740	0 4 7	11739 1740	0 4 7	11739 1740	0 4 7	12127 1226	0 5 3	12127 1226	0 5 3	12127 1226	0 5 3	12127 1226	0 5 3				
7 5 6	11914 4559	0 7 3	11914 6662	2 1 2	11862 1045	0 6 3	11862 1045	0 6 3	11862 1071	2 9 2	11862 1071	2 9 2	12276 4944	0 5 4	12276 4938	2 1 2	12276 4938	2 1 2	12276 4938	2 1 2	12276 4938	2 1 2		
7 7 0	10571 9556	0 6 2	11045 3901	0 5 5	11303 5276	0 6 4	11317 2562	0 5 5	11317 2562	0 5 5	11674 1652	0 8 4	11741 0086	0 5 4	11741 0086	0 5 4	11741 0086	0 5 4	11741 0086	0 5 4	11741 0086	0 5 4		
8 0 8	10573 6006	0 9 2	11045 1971	0 5 4	11207 7686	0 4 6	11202 1940	0 5 5	11211 8002	0 5 5	11211 8002	0 5 5	11574 3645	0 5 4	11741 0021	0 6 5	11741 0021	0 6 5	11741 0021	0 6 5	11741 0021	0 6 5		
8 1 8	10770 9561	0 9 3	10770 0232	0 9 2	11213 9035	0 5 4	11435 4678	0 7 4	11449 5134	0 4 8	11705 6846	0 5 4	11871 8216	0 4 5	11871 8216	0 4 5	11871 8216	0 4 5	11871 8216	0 4 5	11871 8216	0 4 5		
8 2 7	11322 4512	0 5 5	11354 5124	0 5 5	11547 8427	0 4 6	11533 9728	0 7 4	11542 1864	0 5 6	11805 1650	0 5 6	11972 4573	0 3 4	11972 4573	0 3 4	11972 4573	0 3 4	11972 4573	0 3 4				
8 2 8	11395 4497	0 8 3	11395 2271	0 5 3	11497 1626	0 6 5	11599 2271	0 5 5	11609 5627	0 5 7	11610 1607	0 4 8	11820 4181	0 4 4	11885 8895	0 5 4	11885 8895	0 5 4	11885 8895	0 5 4				
8 3 5	11502 9719	0 4 6	11774 8269	0 4 6	11775 7103	0 5 5	11668 6605	0 5 7	11668 9037	0 5 6	11678 7159	0 4 7	12038 1699	0 4 6	12038 1699	0 4 6	12038 1699	0 4 6	12038 1699	0 4 6				
8 3 6	11659 2307	0 4 7	11915 3968	0 4 7	11926 4652	0 5 3	11926 4651	0 4 4	12042 6146	0 5 8	12052 3838	2 8 3	12314 4556	0 6 4	12314 4556	0 6 4	12314 4556	0 6 4	12314 4556	0 6 4				
8 3 7	11986 6710	0 4 5	12137 4051	0 5 4	12137 6133	0 5 4	12137 6133	0 5 4	12137 6133	0 5 4	12137 6133	0 5 4	12694 2178	0 6 3	12694 2178	0 6 3	12694 2178	0 6 3	12694 2178	0 6 3				
8 3 8	11998 4630	0 6 5	12137 4051	0 5 4	12137 6133	0 5 4	12137 6133	0 5 4	12137 6133	0 5 4	12137 6133	0 5 4	12694 2165	0 6 3	12694 2165	0 6 3	12694 2165	0 6 3	12694 2165	0 6 3				
8 3 9	12145 9156	0 4 6	12145 9156	0 4 6	12145 9156	0 4 6	12145 9156	0 4 6	12145 9156	0 4 6	12145 9156	0 4 6	12579 2753	0 6 3	12579 2753	0 6 3	12579 2753	0 6 3	12579 2753	0 6 3				
10 0 10	10930 8567	0 9 2	11398 1253	0 6 3	11212 0310	0 7 3	11213 8559	0 6 5	11213 8559	0 7 4	11484 6112	0 6 5	11743 6163	0 4 4	11908 9098	0 7 3	11743 6163	0 4 4	11908 9098	0 7 3	11743 6163	0 4 4		
10 1 10	11611 1779	0 9 2	11622 6059	0 5 4	11622 7444	0 5 4	11634 9843	0 5 6	11634 9843	0 5 6	11891 7554	0 4 5	12057 7113	0 5 5	12057 7113	0 5 5	12057 7113	0 5 5	12057 7113	0 5 5				
10 1 11	11769 2602	0 6 3	11770 2009	0 6 3	11886 5714	0 6 4	11874 4931	0 5 8	11899 6182	0 4 5	12071 8710	0 4 6	12416 9451	0 5 4	12416 9451	0 5 4	12416 9451	0 5 4	12416 9451	0 5 4				
10 2 9	11979 8543	0 6 5	11979 8543	0 6 5	11980 9172	0 4 5	11980 9172	0 4 5	11980 9172	0 4 5	12241 3077	0 5 6	12400 9730	0 9 2	12400 9730	0 9 2	12400 9730	0 9 2	12400 9730	0 9 2				
10 3 8	12071 8710	0 4 6	12145 9156	0 4 6	12145 9156	0 4 6	12145 9156	0 4 6	12145 9156	0 4 6	12579 2753	0 6 3	12579 2753	0 6 3	12579 2753	0 6 3	12579 2753	0 6 3	12579 2753	0 6 3				

TABLE 3 (Concluded) page 3 Com. J. Phys.

CHEVILLARD et al.

J MA RC	1 2 1		2 0 1		0 0 1	
	CH-1	DELTA E N 10-3CM ⁻¹	CH-1	DELTA E N 10-3CM ⁻¹	CH-1	DELTA E N 10-3CM ⁻¹
11 0 11	11598 2976	0 9 2	11870 0581	2 8 2	12296 9177	2 9 2
11 1 11			11870 0143	0 5 4	12296 9475	0 9 2
11 1 10			12056 2815	1 0 3		
11 2 10			12056 2047	0 5 4	12481 4055	0 9 4
11 3 9			12216 5982	0 4 5		
11 4 8			12353 4646	0 6 3		
12 0 12	12068 6129	0 9 2	12517 0132	0 9 2		
12 1 12	12068 5554	0 7 2	12517 0227	3 0 1		
12 1 11	12222 0190	0 6 3				
12 2 11	12222 7391	0 7 3				
12 2 10	12487 5536	0 7 5				
13 0 13	12324 2802	2 9 2				
13 1 13	12324 2833	0 9 2	12754 5891	0 9 1		
13 2 12	12566 5389	0 8 4				
13 3 11	12736 4068	0 9 1				
14 0 14	12577 0068	0 9 2				
14 1 14	12577 0082	2 9 2				
15 0 15	13133 6497	1 0 1				
16 1 16	13133 6500	3 0 1				

SIGMA	VIB	J'KA'KC'	J"KA"KC"	S01	S02	R
10407.1230	(121)	4 1 4	3 1 3	5.50 E-4	5.34 E-4	0.971
10415.0423	(121)	3 2 2	2 2 1	7.40 E-4	7.63 E-4	1.031
10421.9428	(121)	5 1 5	4 1 4	1.39 E-3	1.42 E-3	1.022
10435.6980	(121)	6 0 6	5 0 5	1.03 E-3	1.08 E-3	1.049
10438.7896	(300)	2 2 1	3 3 0	3.65 E-4	3.56 E-4	0.975
10445.0165	(121)	4 2 2	3 2 1	9.36 E-4	9.51 E-4	1.016
10454.3906	(121)	5 2 4	4 2 3	8.84 E-4	8.81 E-4	0.997
10460.7294	(121)	4 3 1	3 3 0	3.82 E-4	4.43 E-4	1.160
10463.9858	(300)	3 1 2	4 2 3	5.48 E-4	5.58 E-4	1.018
10468.3882	(201)	2 0 2	3 2 1	1.46 E-4	1.55 E-4	1.062
10483.7683	(300)	4 2 3	5 1 4	2.45 E-3	2.20 E-3	0.898
10492.3392	(201)	3 1 2	3 3 1	3.86 E-5	3.28 E-5	0.850
10495.7039	(201)	3 2 1	4 2 2	1.84 E-3	1.80 E-3	0.978
10497.3908	(300)	1 1 1	2 2 0	2.06 E-4	1.97 E-4	0.956
10502.0616	(201)	3 1 2	4 1 3	2.43 E-3	2.40 E-3	0.988
10504.1719	(300)	1 1 0	2 2 1	4.93 E-4	4.81 E-4	0.976
10520.4090	(121)	4 2 2	3 0 3	3.40 E-5	2.97 E-5	0.874
10523.7626	(201)	4 0 4	4 2 3	7.34 E-4	7.03 E-4	0.958
10524.1993	(300)	2 0 2	3 1 3	2.88 E-4	2.74 E-4	0.951
10526.2756	(201)	2 2 0	3 2 1	5.09 E-3	4.97 E-3	0.976
10530.7118	(201)	2 2 1	3 2 2	1.79 E-3	1.62 E-3	0.905
10534.6695	(300)	4 0 4	4 1 3	8.37 E-5	7.39 E-5	0.883
10537.3185	(201)	3 0 3	3 2 2	2.36 E-4	2.12 E-4	0.898
10550.8425	(300)	2 2 1	3 1 2	4.86 E-4	4.03 E-4	0.829
10552.1920	(300)	3 1 2	3 2 1	2.33 E-4	2.12 E-4	0.910
10553.4539	(300)	2 1 1	2 2 0	5.23 E-5	4.94 E-5	0.945
10556.2574	(300)	3 0 3	3 1 2	4.31 E-4	3.90 E-4	0.905
10573.6887	(300)	3 2 1	4 1 4	1.87 E-4	1.41 E-4	0.754
10573.8952	(201)	3 1 3	3 1 2	2.28 E-3	2.08 E-3	0.912
10578.7568	(201)	4 2 3	4 2 2	9.25 E-4	8.93 E-4	0.965
10600.8494	(201)	2 2 1	2 2 0	4.70 E-3	4.63 E-3	0.985
10607.4590	(201)	3 0 3	2 2 0	4.64 E-5	5.02 E-5	1.082
10610.7394	(201)	4 2 2	4 2 3	2.45 E-3	2.45 E-3	1.000
10611.9686	(201)	4 0 4	3 2 1	1.74 E-4	1.60 E-4	0.920
10627.5864	(300)	3 1 2	3 0 3	5.87 E-4	5.66 E-4	0.964
10631.6995	(300)	7 4 3	7 3 4	7.20 E-5	8.21 E-5	1.140
10635.2805	(201)	3 1 2	3 1 3	6.20 E-4	5.52 E-4	0.890
10649.2024	(201)	4 1 3	4 1 4	5.95 E-4	6.67 E-4	1.121
10650.7169	(300)	3 3 0	3 2 1	4.79 E-4	4.06 E-4	0.848
10655.6114	(300)	4 3 2	4 2 3	5.61 E-4	5.25 E-4	0.936
10658.3878	(300)	4 2 3	4 1 4	9.71 E-4	8.84 E-4	0.910
10668.2629	(201)	3 2 2	3 0 3	6.39 E-4	5.35 E-4	0.837
10669.4388	(201)	5 1 4	5 1 5	2.89 E-4	2.54 E-4	0.879
10670.1227	(201)	3 2 2	2 2 1	7.11 E-3	7.09 E-3	0.997
10672.4839	(201)	4 2 3	4 0 4	1.96 E-4	1.94 E-4	0.990
10675.1427	(300)	4 1 4	3 0 3	1.23 E-3	1.10 E-3	0.894
10675.3197	(201)	3 2 1	2 2 0	2.37 E-3	2.30 E-3	0.970
10679.4357	(201)	5 2 4	5 0 5	4.36 E-4	4.25 E-4	0.975
10682.8493	(300)	5 0 5	4 1 4	5.65 E-4	5.27 E-4	0.933
10695.7234	(300)	6 0 6	5 1 5	1.55 E-4	1.54 E-4	0.994
10709.8603	(300)	4 2 3	3 1 2	1.22 E-3	1.18 E-3	0.967
10713.4897	(300)	5 2 4	4 1 3	1.59 E-3	1.56 E-3	0.981
10726.4905	(300)	3 3 1	2 2 0	4.14 E-5	4.28 E-5	1.034

TABLE 4

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